Heating rate effects on thermal analysis measurement of $T_g$ in composite materials

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To cite this article: Ana X. H. Yong, Graham D. Sims, Samuel J. P. Gnaniah, Stephen L. Ogin & Paul A. Smith (2017) Heating rate effects on thermal analysis measurement of $T_g$ in composite materials, Advanced Manufacturing: Polymer & Composites Science, 3:2, 43-51, DOI: 10.1080/20550340.2017.1315908

To link to this article: http://dx.doi.org/10.1080/20550340.2017.1315908
Introduction

Cure assessment is important when optimizing cure efficiency during the manufacture of composite materials. Measurement of the glass transition temperature ($T_g$) is widely used as an indicator of the degree of cure, but present standards cover a number of techniques for its determination, which are known to yield different values for the same material. Thermal lag is one effect that can compromise measured $T_g$ values because of the temperature differential between the thermocouple which provides the temperature output beside the specimen and the temperature within the specimen. As the oven temperature is ramped continuously throughout the test, the specimen temperature lags behind.

A new test method was introduced in standard ISO 6721-11, which serves to correct for the effect of thermal lag in dynamic mechanical analysis (DMA) measurements. This new procedure, whereby different specimens are tested over a range of heating rates, has been used in order to eliminate the effects of thermal lag and determine a $T_g$ independent of heating rate ($T_g(0)$). It has been shown that for measurements of $T_g(0)$ for composites, the DMA thermal lag “corrected” method gave the most reliable data. The work has provided additional guidance on these techniques that could useful be incorporated in future standards, to improve precision, comparisons, and consistency of $T_g$ measurement.

Materials and measurement techniques

Materials

Three types of fiber-reinforced epoxy resin system (Systems A, B, and C) were used to study the effects of specimen thickness, degree of cure, and fiber reinforcement on thermal analysis measurements. A new test method was introduced in standard ISO 6721-11, which serves to correct for the effect of thermal lag in dynamic mechanical analysis (DMA) measurements. This new procedure, whereby different specimens are tested over a range of heating rates, has been used in order to eliminate the effects of thermal lag and determine a $T_g$ independent of heating rate ($T_g(0)$). It has been shown that for measurements of $T_g(0)$ for composites, the DMA thermal lag “corrected” method gave the most reliable data. The work has provided additional guidance on these techniques that could useful be incorporated in future standards, to improve precision, comparisons, and consistency of $T_g$ measurement.

present study, this new method has been applied to DMA, and extended to thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). The aim is to clarify how changes in applied heating rate can affect the thermal analysis and cure measurement of polymer matrix composites, as well as investigating the relationship between these three techniques commonly used in industry, and other testing aspects (e.g. specimen thickness).

Key points

- Cure assessment is important for optimizing cure efficiency during the manufacture of composite materials.
- Measurement of the glass transition temperature ($T_g$) is widely used as an indicator of the degree of cure, but present standards cover a number of techniques for its determination, which are known to yield different values for the same material.
- Thermal lag is one effect that can compromise measured $T_g$ values because of the temperature differential between the thermocouple which provides the temperature output beside the specimen and the temperature within the specimen.
- A new test method was introduced in standard ISO 6721-11, which serves to correct for the effect of thermal lag in dynamic mechanical analysis (DMA) measurements.
- This new procedure, whereby different specimens are tested over a range of heating rates, has been used in order to eliminate the effects of thermal lag and determine a $T_g$ independent of heating rate ($T_g(0)$).
- It has been shown that for measurements of $T_g(0)$ for composites, the DMA thermal lag “corrected” method gave the most reliable data.
- The work has provided additional guidance on these techniques that could useful be incorporated in future standards, to improve precision, comparisons, and consistency of $T_g$ measurement.

Abstract

Three measurement techniques used to measure the glass transition temperature ($T_g$) have been subjected to a critical comparison: dynamic mechanical analysis (DMA), thermomechanical analysis, and differential scanning calorimetry. A new procedure, whereby different specimens are tested over a range of heating rates, has been used in order to eliminate the effects of thermal lag and determine a $T_g$ independent of heating rate ($T_g(0)$). It has been shown that for measurements of $T_g(0)$ for composites, the DMA thermal lag “corrected” method gave the most reliable data. The work has provided additional guidance on these techniques that could usefully be incorporated in future standards, to improve precision, comparisons, and consistency of $T_g$ measurement.

Keywords

Thermal analysis, Cure monitoring, Glass transition temperature, Polymer composites

Cite this article

temperatures. The panels were held for two hours at 150, 160, 170, and 180 °C following a 3 °C/min heating rate to produce four panels at different states of cure. The panels were 300 mm × 300 mm in area, with a cured panel thickness of 2 mm. Prior to testing, System B test specimens were dried for seven days at 80 °C and stored in a controlled environment at 23 ± 2 °C and 50 ± 5% relative humidity.

System C materials were manufactured using prepregs of the same commercial epoxy resin reinforced with either five-harness satin weave carbon-fiber cloth of fiber areal weight 285 g/m², or a four-harness satin weave glass-fiber cloth of fiber areal weight 109 g/m². The prepregs were cut to 300 mm × 300 mm prior to lay-up. The CFRP and GFRP panels were produced using 15 plies and 40 plies, respectively, with cured laminate thicknesses of 3.75 ± 0.2 mm. All panels were cured together using the autoclave cycle recommended by the manufacturer (i.e. temperature ramped at 3 °C/min to an initial hold temperature of 110 °C for one hour, subsequently raised to 180 °C at 3 °C/min and held for two hours). The majority of the specimens were stored under ambient conditions and a single set of DMA specimens were dried at 80 °C before testing. The System C group of materials also included a 30 mm × 15 mm × 3.5 mm plate of the same epoxy resin (unreinforced), which was cured for two hours at 180 °C following a ramp rate of 0.5 °C/min from ambient (23 °C) to 180 °C.

Measurement techniques

Three thermal analysis methods have been used for comparison. Firstly, DMA has been undertaken using a TA Instruments Q800 dynamic mechanical analyzer, according to ISO 6721-11. Figure 1 shows a characteristic DMA output. The relationships shown in the box in Figure 1 are used to calculate the tan delta, loss (viscous) modulus, and storage (elastic) modulus, which are calculated by the instrument software from the stress and strain data, and the phase difference between them. The Q800 instrument employs an optical encoder to measure the displacement (which the instrument software converts to strain) throughout the test. The T_g is often obtained from either: (1) the peak of the loss modulus; (2) the peak of the tan delta curve; or, (3) the inflection point in the storage modulus curve (sometimes the onset of the drop in storage modulus is used), as indicated in Figure 1. Specimens tested were 10 mm × 35 mm (w × l) with different thicknesses in the range 0.25–4 mm; specimens were tested using a single cantilever beam configuration with fibers (unidirectional or woven) parallel to the length of the specimen. For each test, the instrument was set to equilibrate at 30 °C prior to the heating cycle. Specimens were heated at a rate of 3, 5, or 10 °C/min to a final temperature of 180 °C for System A, 250 °C for System B, and 300 °C for System C. The final test temperatures for each material were selected based on the T_g measurement obtained from an initial test in which a specimen was heated at a ramp rate of 10 °C/min to a final test temperature of 350 °C, or lower if the test temperature had clearly passed through the specimen T_g. The final temperature selected for the subsequent runs was set to at least 50 °C above the nominal T_g of the material, as outlined in ISO 6721-11. A frequency of 1 Hz and oscillation amplitude of 10 μm were used, and tests were carried out in static air. The measured T_g was plotted against heating rate and the results extrapolated in order to determine the T_g for zero heating rate, T_g(0), following the standard ISO 6721-11. In addition, the heating rate dependence for each material system was determined from the slope of the data in each case (see Figure 2).

TMA measurements were performed for System B materials using a TA Instruments Q400 thermomechanical analyzer in expansion mode. During the test, the linear movement of a probe, located on the specimen, was used to measure the dimension change via an LVDT; when the expansion is plotted against temperature, the T_g is identified as a point within this transition region. Following the analysis method outlined in ISO 11359-2:1999, the T_g was taken as the midpoint of the transition region, using the first derivative of the dimension change with temperature as a means of indicating the limits of the transition, as shown in Figure 3. In order to identify the T_g, the major dimension change, and the onset and end of
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this major change were identified with the aid of the derivative. Figure 4 shows an example where the end of the major dimension change is the peak in the derivative (at 214 °C in this case), and the onset is the change in slope of the derivative (at 198 °C). The $T_g$ was then taken to be at the midpoint of these two measurements (in this case, at 207 °C). This technique could be applied to all measurements and provided a consistent measurement of $T_g$. The TMA specimens (length, width, and thickness: 10 mm × 10 mm × 2 mm) were tested in the through-thickness direction using a preload force of 0.05 N, which ensures good contact between the probe and the specimen. Following equilibration at 30 °C, Series A and B specimens were heated to 150 and 250 °C, respectively, at a rate of 3, 5, or 10 °C/min. The thermal lag approach was then applied to find $T_g(0)$ for both series.

The DSC measurements of $T_g$ and degree of cure were made using a TA Instruments Q2000. The instrument was calibrated using an indium temperature reference standard (NIST 2232) and a nitrogen gas at a flow rate of 50 ml/min was used in every test. In DSC, $T_g$ was observed as a deviation in the heat flow to the specimen as it undergoes a change in heat capacity. In order to measure the $T_g$, specimens were heated from 30 to 250 °C using a heating rate of 5, 10 or 20 °C/min. Higher heating rates than those employed for DMA and TMA were used, following guidance set out in ISO 11357-2:2014.6,13 The $T_g$ was taken as the inflection point of the heat flow curve as shown in the example plot in Figure 6; again, the thermal lag approach was adopted to find $T_g(0)$.

The DSC measurements of $T_g$ and degree of cure were made using a TA Instruments Q2000. The instrument was calibrated using an indium temperature reference standard (NIST 2232) and a nitrogen gas at a flow rate of 50 ml/min was used in every test. In DSC, $T_g$ was observed as a deviation in the heat flow to the specimen as it undergoes a change in heat capacity. In order to measure the $T_g$, specimens were heated from 30 to 250 °C using a heating rate of 5, 10 or 20 °C/min. Higher heating rates than those employed for DMA and TMA were used, following guidance set out in ISO 11357-2:2014.6,13 The $T_g$ was taken as the inflection point of the heat flow curve as shown in the example plot in Figure 6; again, the thermal lag approach was adopted to find $T_g(0)$.

Figure 3 Schematic showing TMA analysis; the $T_g$ is the midpoint of the transition. The onset and end of the transition seen in the derivative can be used to facilitate identification of the $T_g$.

Figure 4 Schematic diagram for TMA results showing use of the derivative dimension change with temperature to identify the major transition.

Figure 5 Schematic diagram for DSC data showing the inflection point usually taken to be the $T_g$ and the area under the exothermic peak which gives the heat of reaction, $H$, used to calculate the degree of cure.

Figure 6 Schematic showing the limits for analysis of midpoint taken from sharpest signal change seen in derivative.
Following ISO 14322:2012, the degree of cure was measured using the exothermic peak in the DSC measurement of heat flow. The uncured prepreg was heated at 5 °C/min to 300°C to obtain the total heat of reaction (Figure 5). The degree of cure of the material was calculated using Equation (1).  

\[
\text{Degree of cure (\%)} = \left(1 - \frac{H_T}{H_S}\right) \times 100
\]  

where \(H_T\) is the heat of reaction of the specimen being assessed (not shown in Figure 5) and \(H_S\) is the total heat of reaction obtained from measurements performed on the uncured prepreg.

Cured specimens were cut to approximately 2 mm × 2 mm × 2 mm to fit the TA Instruments Tzero crucibles and smoothed using wet and dry paper to optimize contact with the base of the crucible, and therefore with the thermocouple. Uncured prepreg specimens were similarly cut to 2 mm × 2 mm squares. Thermal contact between prepreg layers was ensured through natural tack and local compression provided by the TA instrument’s crucible press. The masses of polymer matrix equated to 0.3–0.4 of the total sample masses, which were in the range 2–10 mg for prepreg and 5–25 mg for the cured material, depending upon the practicalities of ensuring good contact with the crucible.

**Results and discussion**

**Thickness effects on the measurement of \(T_g\) (System A materials)**

Figure 6(a)–(e) show the measured \(T_g\) values against heating rate for each of the five thicknesses of the System A materials using the three common analysis points; the storage modulus inflection point, the peak of the loss modulus, and the peak of the tan delta curves. The data show that the peak of the tan delta curves.

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![Figure 6](image-url)

**Figure 6**  a–e. New procedure using multiple heating rates applied to \(T_g\) measurement by DMA for specimens of thicknesses (a) 0.25 mm (b) 0.5 mm (c) 1 mm (d) 2 mm, and (e) 3.5 mm
Further interrogation of the System A materials provides information on the material and the thermal lag effect. Figure 8 shows the storage modulus inflection point data for all of the specimen thicknesses compared on one graph, indicating that the different thicknesses of material can clearly be separated in terms of $T_g$. This observation has been independently verified by the TMA and DSC test data shown in Table 1. The difference is large enough to be a concern to end-users and product design insofar as these materials were supplied as nominally identical – albeit of different thicknesses. The observation that the results in Figure 7 fall onto one line, regardless of $T_g$, suggests that the heating delta curve gives the highest value of $T_g$ with respect to the other two analysis points; the same relative values of $T_g$ have been described in other work, though not for tests at different thicknesses. For laminate thicknesses of 1 mm and above, the storage and loss moduli give the same value of $T_g$. For thicknesses below 1 mm (i.e., at 0.25 and 0.5 mm specimen thicknesses), the quality of the data was compromised due to significant noise, indicating that the DMA test method using this flexural mode is not suitable for these specimen thicknesses. The results indicate that the inflection of the storage modulus is the best choice for analysis as it provides the least scatter, and therefore the most reliable data.

Gradients of the graphs in Figure 6(a)–(e) are shown plotted against specimen thickness in Figure 7 for the three measurement points. The data show that the degree of thermal lag is dependent on specimen thickness. The smallest specimen thickness (0.25 mm) does not appear to follow the trend closely, but there is more noise in the results for the thinner specimens; DMA testing in tension, as opposed to flexure, could provide a better alternative and give more consistent data for very thin specimens. Figure 7 suggests a potential normalization of data for different thicknesses using a “calibration curve” of this type.

Table 1: Comparison of $T_g$ Values for System A materials by DMA, TMA, and DSC

<table>
<thead>
<tr>
<th>Specimen Thickness</th>
<th>DMA</th>
<th>TMA</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 mm</td>
<td>75.6</td>
<td>Too thin for test</td>
<td>62.5</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>79.4</td>
<td>Too thin for test</td>
<td>65.0</td>
</tr>
<tr>
<td>1 mm</td>
<td>113.5</td>
<td>107.2</td>
<td>103.4</td>
</tr>
<tr>
<td>2 mm</td>
<td>113.1</td>
<td>97.1</td>
<td>106.5</td>
</tr>
<tr>
<td>3.5 mm</td>
<td>72.0</td>
<td>63.4</td>
<td>66.2</td>
</tr>
</tbody>
</table>

Further interrogation of the System A materials provides information on the material and the thermal lag effect. Figure 8 shows the storage modulus inflection point data for all of the specimen thicknesses compared on one graph, indicating that the different thicknesses of material can clearly be separated in terms of $T_g$: 112–125 °C for the 1 and 2 mm material, and 70–85 °C for the 0.25, 0.5, and 3.5 mm material. This observation has been independently verified by the TMA and DSC test data shown in Table 1. The difference is large enough to be a concern to end-users and product design insofar as these materials were supplied as nominally identical – albeit of different thicknesses. The observation that the results in Figure 7 fall onto one line, regardless of $T_g$, suggests that the heating
heating rate dependence is a consequence of the thermal lag in the test, which is dominated by the thermophysical properties of the specimen, as opposed to the \( T_g \), which is a property of the matrix resin. It is likely that the thermal lag effect is dependent on the material diffusivity as DMA specimens are tested under dynamic conditions and the important physical feature in this test is the rate at which heat permeates through the material.

The difference in \( T_g \) that is observed between values measured by DMA, TMA, and DSC in Table 1 can be attributed to the fact that each technique measures a different physical property, where TMA shows changes in free volume due to chain movement, DSC measures calorimetric changes and DMA measures mechanical changes.\(^6,18,19\) These changes could begin/be measurable at different temperatures.

**Cure effects on \( T_g \) measurements (System B materials)**

The DMA results for the System B materials cured to four different states of cure are shown in Figure 9 where there is an expected increase in \( T_g(0) \) with increased cure temperature. The heating rate dependence of the specimens at the four cure temperatures are very similar, giving further indication that the thermal lag effect is dependent on the specimen thermophysical properties, and not on the \( T_g \).

The \( T_g \) measured by TMA and by DSC are plotted against heating rate in Figures 10 and 11 for Series B material specimens. For both techniques, the heating rate dependence appears to be negligible for all of the cure conditions (except, perhaps, for the DSC result for the 170 °C cure). This suggests that both techniques are less sensitive to the effects of thermal lag, possibly because of the smaller specimen sizes used for TMA and DSC, when compared to DMA. For all three measurement techniques, the \( T_g(0) \) value increases, as expected, with the degree of cure (Figure 12). It is probable that the difference between the values of \( T_g(0) \) for the three techniques is due to fundamental differences in the property changes measured (e.g. calorimetric versus dynamic mechanical). Of the three measurement techniques investigated, DMA offers the greatest signal sensitivity to the glass transition and the \( T_g(0) \) value can be identified after accounting for thermal lag.
DMA testing produced using the new method of testing at a range of heating rates (i.e. compensating for thermal lag) enable the greater sensitivity of DMA to be utilized. The limitations of DSC were also noted by O’Neal et al. who suggested that TMA in flexure would be the preferred technique of measuring \( T_g \). However, the advances in DMA testing produced using the new method of testing at a range of heating rates (i.e. compensating for thermal lag) enable the greater sensitivity of DMA to be utilized.
Effect of fiber reinforcement type on $T_g$ measurement (System C materials)

In these tests, System C materials (CFRP, GFRP, and neat resin specimens), manufactured using the same epoxy resin, were tested using DMA in order to evaluate the effects of fiber reinforcement type on $T_g$. These rate-dependent data were compared with DSC data which were obtained at a single heating rate, 20 °C/min, after previous work on Systems A and B showed that the effect of heating rate was negligible. Figure 13 shows that the $T_g$ values are very similar for the CFRP, GFRP, and resin specimens, with small heating rate differences. Terpilowski et al. found the thermal diffusivity of CFRP to be higher than GFRP, from which it would be expected that the heating rate dependence would be lower for the CFRP specimens (i.e. a reduced thermal lag). However, as noted in Good Practice Guide GPG62, reference specimens made with higher thermal conductivity materials showed a higher heating rate dependence, which may be attributable to detailed material/equipment interactions. Interestingly, the same heating rate dependence was obtained for each specimen type when dried to a constant weight (see Figure 14) as the ambient stored specimens.

Concluding remarks

The results obtained indicate that measuring the $T_g$ using the inflection point of the storage modulus measured by DMA and using the new method of testing different specimens at a range of heating rates, is the preferred method for identifying the $T_g$ of a polymer matrix composite. Sensitivity to the glass transition is higher in the DMA, and a correction procedure is available for the thermal lag effect. The other techniques are either less sensitive (DSC) or more difficult to analyze (TMA). The data obtained for different thicknesses of nominally identical material, suggest that the heating rate dependence of the thermal lag can be normalized using a calibration curve. These studies have provided additional guidance on the application of these techniques that could be usefully incorporated in future standards, as a means to increase precision, comparability, and consistency of $T_g$ measurement.

Acknowledgments

This research was carried out as part of an ongoing Engineering Doctorate in Micro- and Nano Materials Technologies (MiNMaT) at the University of Surrey, funded by EPSRC grant EP/G037388/1 and the industrial sponsor, the National Physical Laboratory.

Funding

This work was supported by the EPSRC [grant number EP/G037388/1].

Disclosure statement

No potential conflict of interest was reported by the authors.

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